

TECHNICAL REPORT ARCCB-TR-98002

**THE EFFECT OF A CURING AGENT AND AN
ACCELERATOR ON THE GLASS TRANSITION
OF BROMINATED AND UNBROMINATED
DIGLYCIDYL ETHER OF BISPHENOL A**

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13. ABSTRACT (Maximum 200 words) Dicyandiamide—a solid with a melting point of 209°C—is one of a unique group of curing agents that are insoluble in epoxy at room temperature. As a curing agent for epoxy resins, dicyandiamide can react through all four nitrogen groups—reacting with the resin at both epoxide and hydroxyl sites. When mixed with either diglycidyl ether of bisphenol A or diglycidyl ether of tetrabromobisphenol A, the formulation is stable enough to be stored for 6 to 12 months. Because dicyandiamide's solubility is low at room temperature, the curing reaction is limited until the temperature increases enough to dissolve the curing agent. To improve the ability to process the resin, an accelerator (such as diuron) can be added to reduce the curing temperature. The curing reaction then proceeds via a complex mechanism that is not dominated by a single reaction. Each compound's effect on the cured material was studied by measuring changes in the glass transition temperature.					
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INTRODUCTION

Epon 828—diglycidyl ether of bisphenol A (DGEBA)—is prepared by reacting epichlorohydrin with Bisphenol A. Adding bromine during the synthesis produces a flame-resistant epoxy resin—diglycidyl ether of tetrabromobisphenol A (DGETBBA), Epon 1123. When formulated with dicyandiamide (dicy), which is a solid at room temperature, the resulting resin system has a long shelf life due to dicy's insolubility in epoxy. The system is stable enough to be stored for 6 to 12 months.

The curing reaction begins when the temperature increases enough to dissolve the curing agent. The curing reaction proceeds via a complex mechanism that is not dominated by a single reaction. However, a key factor is the reaction temperature due to the 209°C melting point of dicyandiamide. This high reaction temperature requires the addition of an accelerator (in this case diuron) to reduce the curing temperature and/or curing time.

This study compared the resins Epon 828 and Epon 1123, which were cured with dicy, by measuring the glass transition temperature (T_g) and by determining the effect of diuron on the resin system. It was found that the addition of bromine to the epoxy structure (Epon 1123) resulted in a significant change in the glass transition temperature of the resin system. It was also found that the glass transition temperature after curing depended on the ratio of curing agent to epoxy for both resins. Adding an accelerator to the formulation also produced a change in the T_g .

EXPERIMENTAL PROCEDURE

Two epoxy resins were studied in this work—diglycidyl ether of bisphenol A (Shell Epon 828-DGEBA) and diglycidyl ether of tetrabromobisphenol A (Shell Epon 1123-DGETBBA). These resins were formulated with dicyandiamide, a curing agent manufactured by the Sigma Chemical Co. The curing reaction was accelerated by using either 0%, 1%, or 2% diuron, an accelerator also manufactured by the Sigma Chemical Co. All the materials were commercial products and were used as received—except for Epon 1123, which was solvated with 18.1% acetone to reduce viscosity. The acetone was removed by heating the resin to 80°C for approximately 30 minutes.

The manufacturer's reference manual lists Epon 828 (DGEBA) as having a repeat unit of $n = 0.2$ for the resin, which was confirmed in the literature. Using a value of 0.2 for n yields a molecular weight of 397.3 g/mole. Because little information could be found in the literature for Epon 1123 (DGETBBA), the same n value was assumed—resulting in a molecular weight of 776.02 g/mole. The molecular weight of dicy is 84.08 g/mole. These values were used to calculate the mole ratios of dicy to epoxy.

Samples were prepared from both resins using various formulations of dicy or dicy and diuron. The samples were weighed, placed in hermetically sealed aluminum pans, and analyzed in a differential scanning calorimeter (DSC) model Perkin-Elmer DSC7. The instrument was

purged with nitrogen, and the samples were scanned at 20°C/minute. The samples containing diuron were initially cured by increasing the temperature from 50°C to 270°C. The samples without diuron were cured by increasing the temperature from 50°C to 350°C. After curing, the samples were again scanned at 20°C, and the glass transition was measured. The T_g was measured by extending the pre- and post-transition baseline and taking the mid-point.

RESULTS AND DISCUSSION

DGEBA and DGETBBA Cured with Dicyandiamide

Before measuring the glass transition, the samples were cured in a DSC—which scanned at a rate of 20°C/minute until the curing process was complete. The samples were then rapidly cooled to room temperature. For the DGEBA samples at the lowest molar ratio of dicy to epoxy, the curing exotherms were broad and symmetric. However, as the molar ratio increased, the exotherms became asymmetric. The DGETBBA curing exotherm for the lowest molar ratio was also broad and symmetric. However, in this case, the exotherms remained symmetric and became sharper as the molar ratio increased. In both cases, a small endotherm began to appear at 209°C as the concentration of curing agent increased. This resulted from the melting of unreacted dicyandiamide.

To measure the T_g, the samples were rescanned after curing at a rate of 20°C/minute. In Table 1, the T_g for DGEBA is 129°C with 0% diuron and a molar ratio of 0.10 for dicy/epoxy. As the molar ratio of the samples increased, the T_g of the samples decreased—reaching a minimum glass transition temperature of 105°C at a molar ratio of 0.27. As the molar ratio continued to increase, the T_g seemed to increase to 115°C; however, it should be noted that the samples prepared from just resin and dicy frequently displayed very small changes in the heat capacity and occasionally displayed standard deviations as large as 12°C.

Table 2 shows that at a molar ratio of 0.09 for DGETBBA and with 0% diuron, the epoxy has a T_g of 60°C. This shows that adding bromine to the epoxy structure resulted in a decrease of approximately 69°C in the T_g. As the molar ratio increased to 0.19, the T_g also increased to 77°C. The T_g continued to increase—reaching a maximum T_g at 119°C. However, the T_g appeared to reach a plateau at a molar ratio of 0.48. Thus, we see that the relationship between the molar ratio and the glass transition for DGETBBA and DGEBA displayed inverse trends.

DGEBA Cured with Dicyandiamide and 1% or 2% Diuron

Adding diuron to the formulation resulted in sharper curing exotherms and an increase in the ΔC_p between the pre- and post-transition baseline for all dicy ratios. Adding 1% diuron to the DGEBA epoxy formulation at the lower molar ratio resulted in a decrease in the T_g (as seen in Table 1 and Figure 1). At a molar ratio of 0.10, the T_g decreased by 6°C for 1% diuron and 9°C for 2% diuron. In all cases, as the molar ratio increased, the T_g decreased; however, the rate of decrease was greatest when no diuron was added to the formulation. Samples containing 1%

diuron had a minimum Tg of 112°C at a molar ratio of 0.38. Samples containing 2% diuron had a minimum Tg of 113°C at a molar ratio of 0.31. As seen in Figure 1, increasing the diuron concentration to 2% produced a small decrease in the Tg, but the curves were almost parallel up to a molar ratio of 0.40. Adding diuron to the formulation also reduced the Tg's sensitivity to changes in the dicy/epoxy molar ratio.

DGETBBA Cured with Dicyandiamide and 1% or 2% Diuron

As seen in Table 2 and Figure 2, adding 1% diuron to the brominated epoxy formulation resulted in the same relationship between molar ratio and Tg that was observed for the 0% diuron case. The Tg at a molar ratio of 0.10 was 54°C for the 1% diuron samples; without diuron, the Tg was 60°C—a change of 6°C. As the molar ratio increased, the Tg for the 1% case increased at a slightly faster rate than the 0% diuron case but reached a peak Tg at approximately the same temperature but at a lower molar ratio—0.29 rather than 0.48.

When the diuron concentration was increased to 2%, the same relationship between the dicy molar ratio and Tg was observed. However, a decrease of approximately 6°C in the maximum Tg (from 117°C to 111°C) was observed.

CONCLUSION

Adding bromine to the DGEBA structure had a profound impact on the Tg of the resin system. The Tg for DGETBBA displayed an inverse relationship to changes in the dicy/epoxy molar ratio. For DGETBBA, the Tg increased as the dicy molar ratio increased; for DGEBA, the Tg decreased as the dicy molar ratio increased. Adding bromine also reduced the maximum Tg for 0%, 1%, or 2% diuron.

In the DGEBA case, adding diuron to the formulation resulted in a significantly slower rate of decrease in the Tg versus the dicy/epoxy molar ratio. At a molar ratio of 0.30, there was a 10°C to 20°C increase in the Tg for the 1% and 2% cases.

For the brominated resin with 1% diuron, the relationship between the dicy/epoxy molar ratio and Tg was not affected much. Increasing the diuron concentration to 2% produced a small decrease in the Tg at most ratios and reduced the maximum Tg by about 7°C.

BIBLIOGRAPHY

1. Aprcella, A., *Journal of Thermal Analysis*, 30, 1979, pp. 137.
2. Lin, Y., Sautereau, H., Pascault, J., *Journal of Polymer Science. Part A: Polymer Chemistry*, 24, 1986, pp. 2171.
3. Lin, Y., Galy, J., Sautereau, H., Pascault, J., *Crosslinked Epoxies*, Walter de Gruyter & Co., Berlin, 1987.
4. *Epon Resin Structural Reference Manual*, Shell Chemical Co., Texas, 1989.
5. Wunderlich, B., *Thermal Analysis*, ATHAS Laboratory Program, New York, 1986.
6. Turi, E.A., *Thermal Characterization of Polymeric Materials*, Academic Press, Inc., Florida, 1981.
7. Wendlandt, W.W., *Thermal Analysis*, 3rd ed., Wiley, New York, 1986.

**Table 1. Glass Transition for DGEBA Cured with
Dicyandiamide and 0%, 1%, or 2% Diuron**

Resin mmoles	Dicy mmoles	Dicy wt %	Dicy/Epoxy molar ratio	DGEBA (Tg °C)		
				0% Diuron	1% Diuron	2% Diuron
8.91	0.90	2.10	0.10	129	123	120
7.90	1.20	3.00	0.15	123	----	----
7.84	1.54	3.92	0.20	108	121	120
10.10	2.50	5.02	0.25	----	120	119
7.83	2.10	5.34	0.27	105	117	----
10.10	3.10	5.99	0.31	----	124	113
10.13	3.40	6.61	0.34	115	----	----
10.10	3.80	7.35	0.38	----	112	114
10.31	7.21	13.02	0.70	----	115	114

**Table 2. Glass Transition for DGETBBA Cured with
Dicyandiamide and 0%, 1%, or 2% Diuron**

Resin mmoles	Dicy mmoles	Dicy wt %	Dicy/Epoxy molar ratio	DGETBBA (Tg °C)		
				0% Diuron	1% Diuron	2% Diuron
5.16	0.48	1.00	0.09	60	54	54
5.16	0.74	1.50	0.14	----	----	77
5.16	0.98	2.01	0.19	77	83	87
5.16	1.50	3.05	0.29	108	117	107
5.16	1.97	3.94	0.39	----	112	111
5.16	2.50	5.00	0.48	118	115	110
5.16	3.09	5.98	0.60	----	----	109
5.18	3.60	7.00	0.70	119	113	110

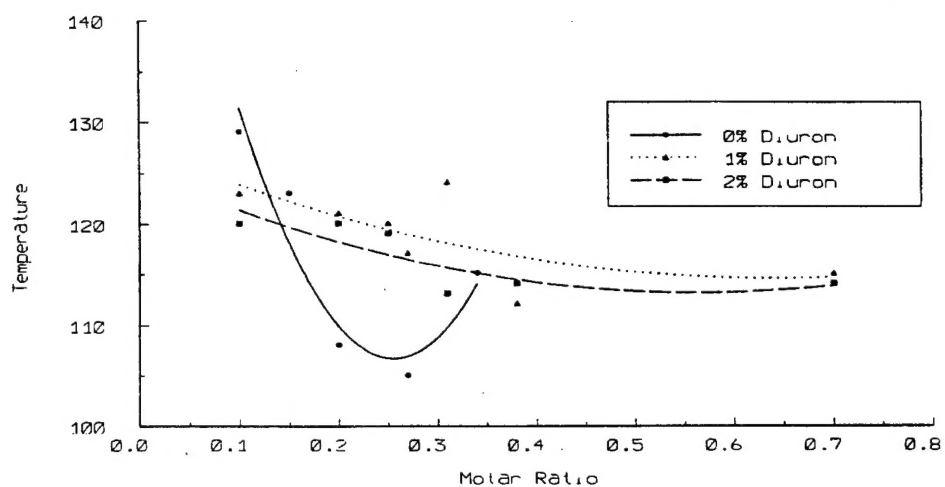


Figure 1. Plot of glass transition vs. molar ratio of Dicy/DGEBA

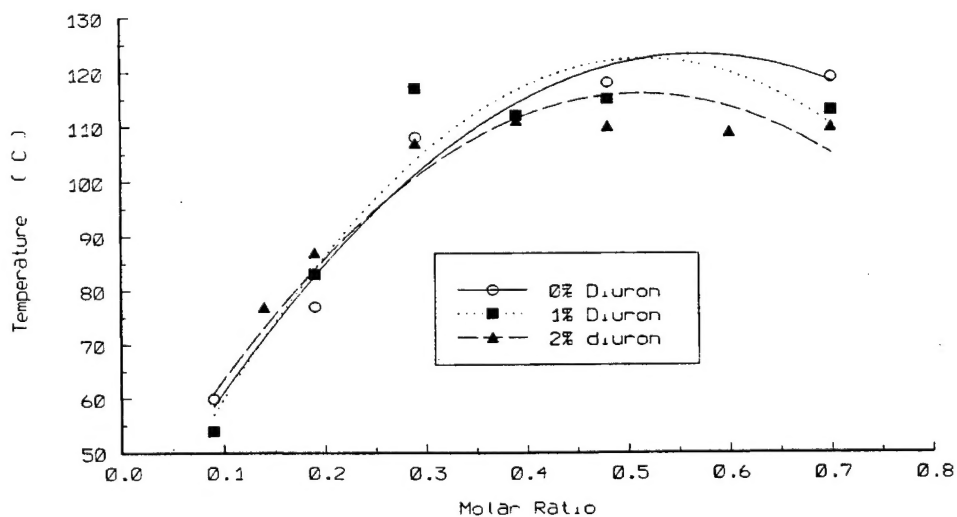


Figure 2. Plot of glass transition vs. molar ratio of Dicy/DGETBBA

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